



Degradation of ionic liquids by Fenton reaction; the effect of anions as counter and background ions

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ARTICLE INFO

Article history:

Received 24 March 2009
Received in revised form 25 June 2009
Accepted 27 June 2009
Available online 3 July 2009

Keywords:

Ionic liquids
Perfluoric acids
Fenton reaction
Oxidation of organic matter

ABSTRACT

The influence of counter ions (Cl^- , $\text{C}(\text{CN})_3^-$ and CF_3SO_3^-) and background ions ($\text{C}_6\text{F}_{11}\text{O}_2^-$, $\text{C}_8\text{F}_{15}\text{O}_2^-$ and $\text{C}_{10}\text{F}_{19}\text{O}_2^-$) on the degradation rates of 1-butyl-3-methylimidazolium cation (bmim^+) in a Fenton-like system were investigated. The degradation rate of bmim^+ was influenced by the particular anions as follows: $\text{Cl}^- > \text{C}(\text{CN})_3^- > \text{CF}_3\text{SO}_3^-$. The inhibition of imidazolium moiety oxidation was observed in the case of counter anions in ionic liquid which entered the competition for hydroxyl radicals with bmim^+ or which formed complexes with ferric and ferrous ions. The presence of perfluoric acids as a background in solution also had significance for the bmim^+ degradation process. These organic anions can inhibit bmim^+ oxidation through strong interactions between positively charged bmim^+ and negatively charged perfluocarboxylic anions (PFCA). Additionally, bmim^+ seemed to be more resistant to oxidation in the presence of a longer n-perfluoric alkyl chain anions. However, it was observed that the inhibition of bmim^+ oxidation decreased when the concentration of PFCA in solution exceeded a critical micellar concentration. This fact can be explained by weaker interactions between bmim^+ and perfluoric anions, stronger associated with aggregated PFCA in these experimental conditions (pH 3). Our investigations also indicated the possibility of PFCA interactions with ferric and ferrous ions.

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1. Introduction

Ionic liquids (ILs) are a class of organic salts that are liquid at or near room temperature. They serve as good solvents for various chemical and electrochemical reactions, are nonvolatile and nonflammable. Therefore, they have been proposed as “green solvents” for chemical reactions and separation processes [1–4]. This wide applicability of ILs is mainly based on their beneficial physico-chemical properties, e.g. high thermal and electrochemical stability, high conductivity, extraction behavior, etc.

The optimization of the properties necessary for the defined technical application of ILs is determined by the high structural variability of cations and corresponding anions. However, regarding the hazard assessment of ILs, this structural variability represents an almost insurmountable problem, as it would be necessary to generate a profound knowledge of the effects on man and on the environment for every single compound. Several authors have already mentioned ecotoxicological influences of ILs on some selected organisms, for example bacteria [5,6], algae [7,8], Q1 waterfeals [9] and zebrafish [10]. The impact of ILs on aquatic ecosystems is highly important as some ILs have a high solubility in water.

The solubility of these ionic liquids in water is strongly dependent on both the length of the alkyl chains attached to the cation and the kind of anion used. Generally, two different types of IL anions are used: fluorous anions such as CF_3SO_3^- , BF_4^- , and non-fluorous anions such as Cl^- , AlCl_4^- , $\text{N}(\text{CN})_3^-$; and there are four main groups of cations: dialkylimidazolium, dialkylpyridinium, dialkylpyrrolidinium and tetraalkylammonium. However, polluted industrial effluents usually contain different organic ions, as well as considerable concentrations of common inorganic ions, which in particular may affect, e.g. the efficiency of their utilization.

Perfluorinated acids (PFCA) and their salts have been widely used in industry as surfactants, lubricants and corrosion inhibitors; they are used as emulsifying agents in polymer synthesis and as surface treatment agents in photolithography. The widespread application, environmental persistence and bio-accumulative potential of perfluorinated compounds results in the global occurrence of these substances in air, sediment, water, animals and humans [11,12]. Perfluorooctanoic acid and its salts, regarded as terminal degraded products, are the chemicals that have frequently been detected in environmental samples and very often occur in high concentrations [13].

Ionic liquids may be used as the solvents in fluorination of organic compounds as well as in the extraction of organic pollutants from water. These facts indicate that ionic liquids could appear in wastewater together with perfluoric compounds,

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and may form new ion pairs to have different physico-chemical and biological properties than the parent compounds.

The removal of harmful organic pollutants from wastewater and soil has been investigated by a variety of chemical processes. Among these processes, one involving Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) has been the subject of numerous investigations into the mechanisms, reaction kinetics and efficiencies of processes for removing organic pollutants [14–17]. The Fenton process depends on electron transfer between H_2O_2 and Fe^{2+} , the latter acting as a homogeneous catalyst [14]. With an oxidizing potential of 2.8 V vs. NHE, these $\cdot\text{OH}$ radicals are capable of oxidizing a wide range of organics in wastewater. The oxidant used in the process is easy to handle and environmentally friendly, as the final decay products (water, oxygen and ferric hydroxide) exert no harmful effect. The performance of a Fenton system is governed mainly by the concentration of hydroxyl radicals produced in the reaction mixtures. The standard Fenton reaction is usually modified by the use of a higher hydrogen peroxide concentration and of different catalysts.

Our previous paper showed that the oxidation rates of imidazolium ionic liquids by Fenton-like reactions ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) are structure-dependent and are correlated with the n-alkyl chain length substituted at the N-1-position [18]. The level of degradation depended on the type of head group, too. In this work we demonstrated that anions, originating from ILs or found in the background, also influence IL degradation efficiency. Additionally, the negatively charged anions can interact with the positively charged catalyst used in Fenton or Fenton-like reactions, and can influence the oxidation process.

2. Materials and methods

2.1. Chemicals

The ionic liquids selected for these studies; 1-butyl-3-methylimidazolium chloride (bmimCl), trifluoromethanesulfonate (bmimCF₃SO₃), and tricyanmethide (bmimC(CN)₃) were purchased from Merck KGaA (Darmstadt, Germany), hydrogen peroxide (30%) from Standard (Lublin Poland), $\text{Fe}(\text{ClO}_4)_3 \times \text{H}_2\text{O}$, $\text{Fe}(\text{ClO}_4)_2 \times \text{H}_2\text{O}$ and o-phenanthroline from Sigma-Aldrich (Buchs, Switzerland), C₆F₁₁O₂H, C₈F₁₅O₂H, C₁₀F₁₉O₂H from ABCR GmbH & Co KG (Shlehert).

The stock solutions of 1-butyl-3-methylimidazolium salt and ferric salt were prepared in deionized water (TOC < 5 ppb, 5 $\mu\text{S}/\text{cm}$) obtained in-house by passing tap water through a carbon filter, then subjecting it to reverse osmosis, and finally passing it through a bed of mixed ion exchangers and a 0.45 μm filter. The stock ionic liquid solutions (0.01 M) were prepared and stored at 4 °C. The ferric perchlorate solution was prepared by dissolving the appropriate weight of $\text{Fe}(\text{ClO}_4)_3 \times \text{H}_2\text{O}$ or $\text{Fe}(\text{ClO}_4)_2 \cdot \text{nH}_2\text{O}$ in 0.01 M HClO₄.

2.2. Oxidation of ionic liquids in the Fenton-like system ($\text{H}_2\text{O}_2/\text{Fe}^{3+}$)

The ionic liquids were oxidized in a dilute aqueous solution (1×10^{-3} M). Experiments were conducted in a well-stirred and thermostated batch reactor (volume = 0.30 L) at 25 ± 1 °C. All reactions were performed in the dark to prevent photoreduction of Fe^{3+} . Reaction mixtures were obtained by taking the appropriate aliquot of ionic liquid stock solution, adding Fe^{3+} , adding perfluoric acid and adjusting the pH with perchloric acid to a value 3.0 or 3.5. The reaction was started by the addition of an appropriate portion of H_2O_2 . During the experiment, samples were collected after various reaction times and immediately quenched with 0.05 M NaOH. The degradation of ionic liquids was stopped after 4 h. All experiments were conducted in duplicate.

2.2.1. Oxidation of perfluorocarboxylic acids in the vigorous Fenton-like system ($\text{H}_2\text{O}_2/\text{Fe}^{3+}$)

The perfluorocarboxylic acids (1×10^{-3} M) were oxidized by Fenton-like reaction, where the concentration of Fe^{3+} was 1×10^{-3} M, dose of H_2O_2 was 400 mM and pH 3.5. After 24 h of degradation sample was collected, quenched with 0.05 M NaOH and studied by ¹⁹F-NMR spectroscopy. Spectra were recorded on a Varian Mercury 400 MHz spectrometer (operating frequencies 376.26 MHz) at 30 °C. Chemical shifts were reported relative to external TFA (δ_F – 78.5). The fluoride concentration was analyzed electrochemically with a fluoride ion-selective, combination electrode (WTW F 800) by use of total ionic strength adjustment buffer (TISAB). The fluoride samples and the fluoride standard solutions were diluted 1:1 with a TISAB.

2.3. Analytical procedures

2.3.1. HPLC analysis of ionic liquids

Details of the analytical procedures for ionic liquids can be found in several recent papers by our team [19–21]. For this study we used a high-performance liquid chromatograph (Perkin Elmer Series 200) consisting of a chromatographic interface (Link 600), binary pump, UV/VIS detector, vacuum degasser and Rheodyne injection valve. The ionic liquids were separated in a Synergi Polar-RP 150 × 4.6 mm column (Phenomenex) packed with polar endcapped particles (4 μm ; pore size 80 Å; specific surface area 1.05 $\text{m}^2 \text{ g}^{-1}$; carbon load 11%; calculated bonded phase coverage 3.15 $\mu\text{mol m}^{-2}$). The analyses were performed at ambient temperature at a flow rate of 0.75 ml min⁻¹, and the elution profiles were monitored at $\lambda = 218$ nm. The separation column was equilibrated with mobile phase until baseline stabilization, at which point the sample injections (10 μl) were made. The mobile phase was methanol or acetonitrile (concentration range 1–52% v/v) mixed with 5 mM phosphate buffer (KH₂PO₄/H₃PO₄) and adjusted to pH 3.

2.3.2. Determination of Fe and H_2O_2

Fe^{2+} was analyzed by o-phenanthroline colorimetry at 510 nm. The molar extinction coefficient of the Fe^{2+} -phenanthroline complex was $1.11 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

Hydrogen peroxide was determined iodometrically ($[\text{H}_2\text{O}_2] > 10^{-3}$ M). The pH was measured with a pH-meter (HACH EC 20) calibrated at 25 °C and using standard buffers (3.0, 4.0 and 7.0).

2.4. Computational method and calculation

These calculations were performed using a Gaussian 03 package program set supplied by Gaussian Inc. [22]. The optimization geometries and atomic charges were calculated using the DFT/B3PW91 method with a 6-311G++ level basis set.

3. Results and discussion

3.1. Oxidation of 1-butyl-3-methylimidazolium ionic liquids with different counter ions

Fig. 1a demonstrates that the rate of decomposition of bmimX, where X is the counter anion in ionic liquid, strongly depends on the nature of X. The decomposition of bmimX showed linearity on a pseudo-first-order plot (Fig. 1b), and this indicates that the reaction follows pseudo-first-order kinetics. As it can be seen in Fig. 1, the rate of oxidation of imidazolium cations was the lowest in the presence of chloride. For bmimC(CN)₃, the degradation rate was observed to be 1.4 times faster than bmimCl. After 150 min both compounds were completely decomposed in experimental conditions. The highest rate degradation was found for bmimCF₃SO₃ for which degradation was complete after 45 min.

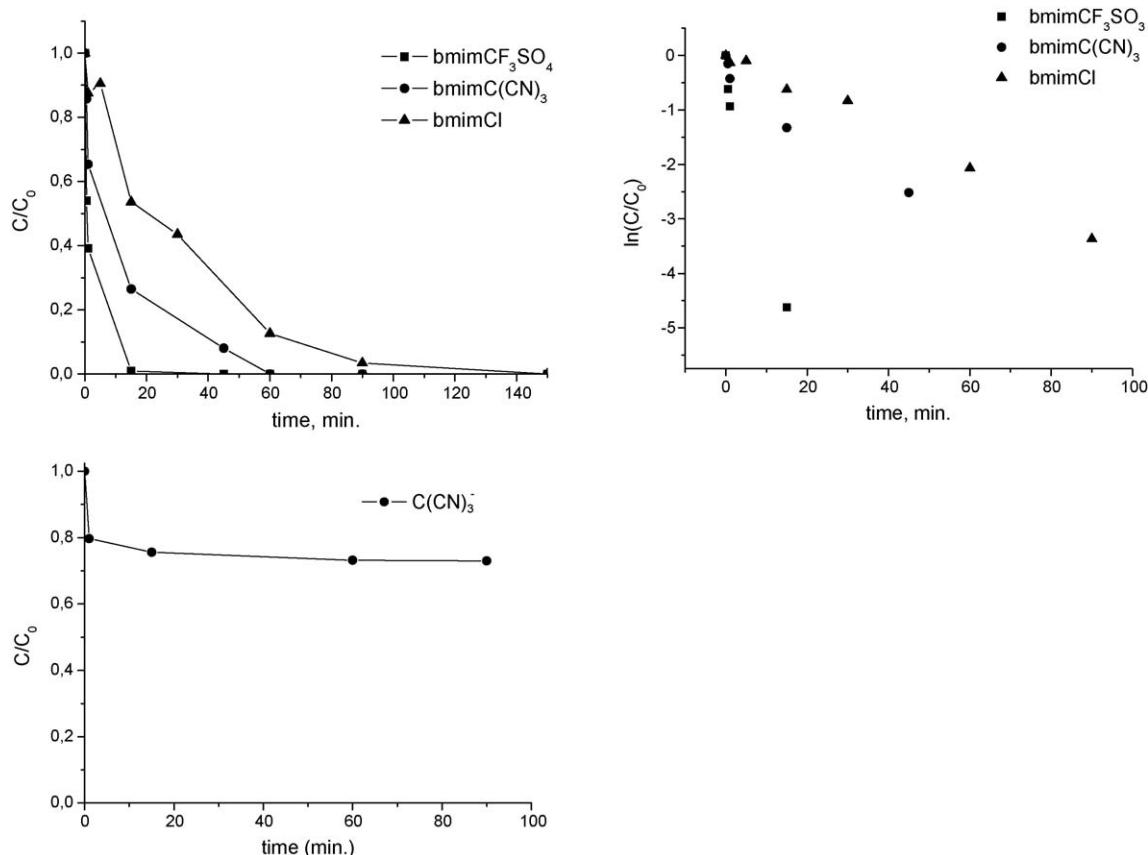


Fig. 1. (a) Changes in the concentration of bmimX during Fenton-like reaction. (b) Pseudo-first-order plots of degradation of bmimX with time. (c) Changes in the concentration of $\text{C}(\text{CN})_3^-$ during $\text{bmimC}(\text{CN})_3$ oxidation by Fenton-like system ($k_{\text{bmimCl}} = 0.036 \text{ min}^{-1}$, $k_{\text{bmimC}(\text{CN})_3} = 0.051 \text{ min}^{-1}$, $k_{\text{bmimCF}_3\text{SO}_4} = 0.285 \text{ min}^{-1}$).

As expected, the lowest rate was obtained in the presence of chloride. This effect has been attributed to (i) a decrease in the rate of generation of hydroxyl radicals, due to formation of chloro- Fe^{3+} complexes which does not take a part in H_2O_2 decay, and (ii) the formation of inorganic radicals Cl_2^{\bullet} , which are less reactive than $^{\bullet}\text{OH}$ [23]. These reactions lead to a decrease in the amount of hydroxyl radicals in solution and consequently to a decrease in the rate of decomposition of imidazolium ionic liquid.

Similarly, to Cl^- , the $\text{C}(\text{CN})_3^-$ counter ion had a significant influence on the rate of degradation of the imidazolium ionic liquid. Fig. 1c demonstrates that in the first 15 min of reaction, 25% of the starting $\text{C}(\text{CN})_3^-$ was lost simultaneously with the oxidation of the imidazolium cation. The smell of almonds suggested that the decomposition of $\text{C}(\text{CN})_3^-$ went in the direction of HCN evolution. This reaction was in competition with the degradation of the imidazolium, and led to a decrease in the amount of hydroxyl radicals accessible for cation oxidation. There was not any observed inhibition of depletion of H_2O_2 by complexation of the catalyst.

CF_3SO_3^- is an anion with a strong delocalization of the negative charge. It is characterized by chemical inertness and weak coordination. We suppose that these physico-chemical properties allow its presence in the reaction mixture to have no significant influence on degradation of imidazolium ionic liquids in Fenton-like system. As expected, the degradation rate of $\text{bmimCF}_3\text{SO}_4$ was the highest.

3.2. Effect of perfluoric acids on the oxidation rate of bmimCl in Fenton system

Perfluorinated acids are known to resist heat, acids and bases, as well as reducing and oxidizing agents. Our objective was the examination of the influence of perfluorocarboxylic ions ($\text{C}_6\text{F}_{11}\text{O}_2^-$,

$\text{C}_8\text{F}_{15}\text{O}_2^-$ and $\text{C}_{10}\text{F}_{19}\text{O}_2^-$) on bmimCl degradation in Fenton reactions. Although it is known that AOP techniques have been applied for the oxidative removal of selected fluorinated compounds, the application of Fenton's reagent failed [24]. Our results also indicate that in a vigorous $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system, mineralization of this compound or the degradation of part of the fluorinated alkyl chain could be excluded, because no fluoride ions were detected and no new peaks appeared in the ^{19}F -NMR spectra of PFCA after 24 h of degradation.

In order to examine the effects of perfluorocarboxylic acids on bmimCl degradation by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, three series of experiments were conducted: (i) oxidation of bmimCl by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ systems in the presence of $\text{C}_6\text{F}_{11}\text{O}_2^-$, (ii) oxidation of Fe^{2+} in the presence of $\text{C}_6\text{F}_{11}\text{O}_2^-$, $\text{C}_8\text{F}_{15}\text{O}_2^-$ and (iii) oxidation of bmimCl by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence of $\text{C}_6\text{F}_{11}\text{O}_2^-$, $\text{C}_8\text{F}_{15}\text{O}_2^-$ and $\text{C}_{10}\text{F}_{19}\text{O}_2^-$.

An inhibitory effect was observed of $\text{C}_6\text{F}_{11}\text{O}_2^-$ on the oxidation of bmimCl by both systems: $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ (Fig. 2). The results in Fig. 2b and c, in contrast to Fig. 2a, show a significant decrease (20%–25%) in the efficiency of bmimCl degradation. Additionally the increased concentration of $\text{C}_6\text{F}_{11}\text{O}_2^-$ from 0.16 to 1.00 mM led to a decrease in oxidation efficiency, yet the effect of the inhibition was not proportional to the increase in $\text{C}_6\text{F}_{11}\text{O}_2^-$ concentration. The lowest inhibition effect was observed for vigorous $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, where $[\text{H}_2\text{O}_2] = 400 \text{ mM}$ (Fig. 2a). This reaction was more vigorous than the standard Fenton system, as the pollutants are oxidized, reduced or attacked by nucleophiles in a single system. The higher concentration of H_2O_2 promotes a series of propagation reactions that produce a perhydroxyl radical, superoxide anion and peroxide anion in addition to a hydroxyl radical. The mix of reactive oxygen species provided a highly reactive matrix that had the potential to transform the organic contaminants to a great extent [25].

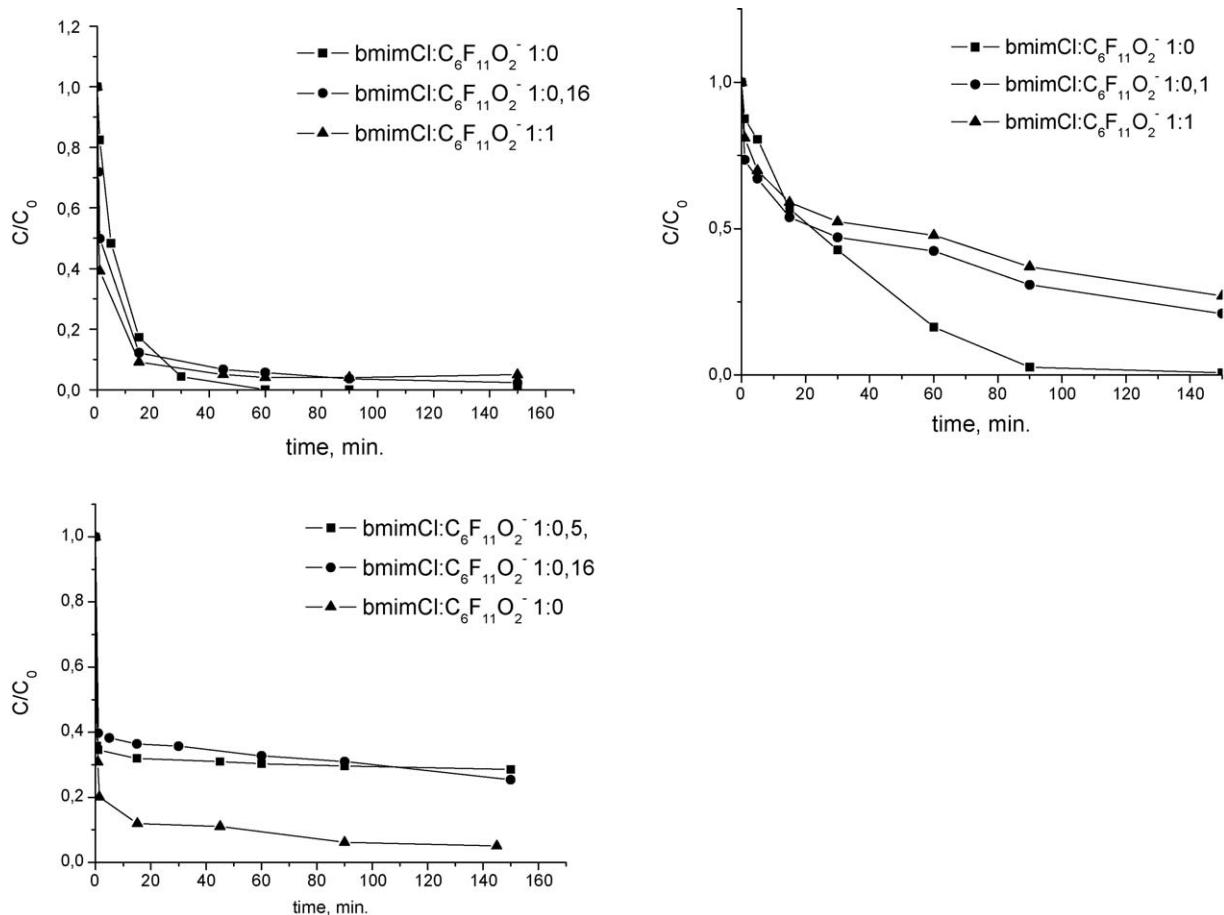


Fig. 2. Decomposition of bmimCl in the presence of $\text{C}_6\text{F}_{11}\text{O}_2\text{H}$ (a) by $\text{Fe}(\text{III})/\text{H}_2\text{O}_2$ where $[\text{Fe}(\text{III})] = 1 \text{ mM}$, $[\text{H}_2\text{O}_2] = 400 \text{ mM}$, pH 3.5 (b) by $\text{Fe}(\text{III})/\text{H}_2\text{O}_2$ where $[\text{Fe}(\text{III})] = 1 \text{ mM}$, $[\text{H}_2\text{O}_2] = 100 \text{ mM}$, pH 3.0 (c) by $\text{Fe}(\text{II})/\text{H}_2\text{O}_2$ where $[\text{Fe}(\text{II})] = 1 \text{ mM}$, $[\text{H}_2\text{O}_2] = 20 \text{ mM}$, pH 3.0.

The data presented in Fig. 3 indicate that in the presence of $\text{C}_6\text{F}_{11}\text{O}_2^-$ or $\text{C}_8\text{F}_{15}\text{O}_2^-$, H_2O_2 has a lower reactivity towards Fe^{2+} . The addition of bmim^+ to the reaction mixture led to an increase in the rate of Fe^{2+} oxidation, but the inhibition of this reaction by PFCA anions was still observed. The inhibition of the oxidation rate of Fe^{2+} suggested that ferrous ions interacted with the perfluorocarboxylic moiety, because the reaction of perfluorocarboxylic acids with hydroxyl

radicals was out of the question (lack of F^- in solution). It is in good agreement with the inhibition of rates of bmimCl degradation by PFCA in Fenton and Fenton-like reactions. In both reactions the Fe^{2+} oxidation plays a key role in OH^\bullet generation. However, the data presented in Fig. 2a and b show a small but significant increase in the rate of bmim^+ oxidation in the first 20 min of the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ process. This fact suggests that perfluorocarboxylic acids may interact with Fe^{3+} ions, moving the equilibrium in reaction (1) to the left side:



The decrease in concentration of the chloro- Fe^{3+} complexes leads consequently to an increase in the rate of decomposition of H_2O_2 . This accelerated Fenton-like reaction improves the degradation of organic matter.

Published results indicate that at a high perfluoro-compounds concentration the stronger binding of tetraethylammonium ions than lithium ions onto the perfluorooctylsulfonate micellar surface occur [26]. Additionally, the unexpected stabilization of the pyridinium ring by the strong dissolution in CF_3COOH was observed and has been discussed in literature [27]. These results permit us presume that bmim^+ can interact with perfluorocarboxylic moiety, and these interactions can also have some influence on the rate of bmimCl degradation. In our case, it is not with the hard ammonium ion, with its high charge density, but rather with the much softer imidazolium ion, where the positive charge is delocalized across several atoms, like in a pyridinium cation.

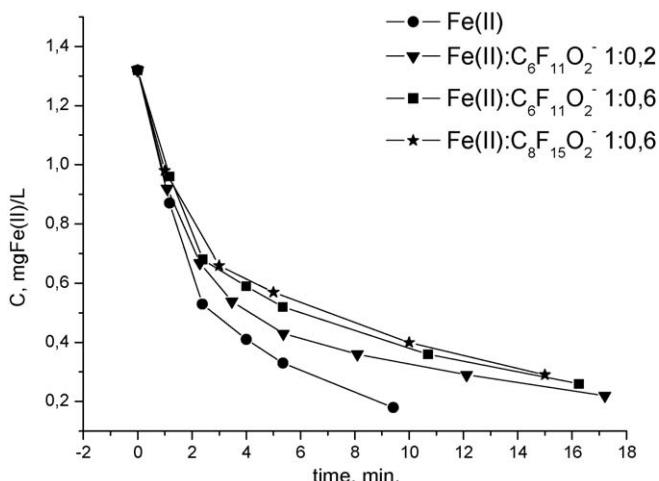


Fig. 3. Oxidation of $\text{Fe}(\text{II})$ by H_2O_2 in the presence of $\text{C}_6\text{F}_{11}\text{O}_2^-$ and $\text{C}_8\text{F}_{15}\text{O}_2^-$ (organic free water $[\text{Fe}(\text{II})]_0 = 1.32 \text{ mgL}^{-1}$, $[\text{H}_2\text{O}_2] = 1 \text{ mM}$, pH 2.5, $T = 25^\circ\text{C}$)

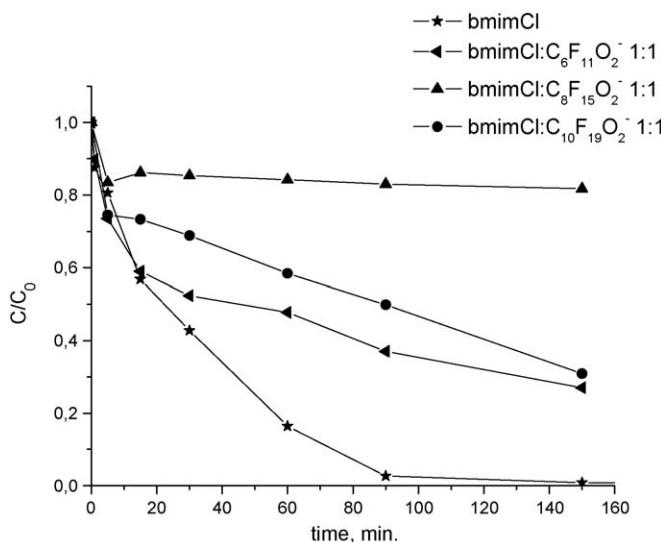


Fig. 4. Concentration-time profile obtained for bmimCl oxidation by Fe(III)/H₂O₂ in presence of different perfluorocarboxylic acids.

The comparison of data from Figs. 3 and 4 shows that even though both C₆F₁₁O₂⁻ and C₈F₁₅O₂⁻ inhibited the oxidation of Fe²⁺ to a similar extent, C₈F₁₅O₂⁻ was a stronger inhibitor of bmimCl degradation. The increase in C₈F₁₅O₂⁻ concentration from 0.1 to 1 mM caused a more significant increase in inhibition of bmimCl oxidation than the increase in C₆F₁₁O₂⁻ concentration (Fig. 5). It suggested that stronger ion-pairing effects are likely to be observed in the presence of longer perfluorocarboxylic anions, and hence have the effects of "stabilizing" the imidazolium cation to a greater extent.

The Fe²⁺ and Fe³⁺ ions are in competition with bmim⁺ for interaction with perfluoric acids. However, carboxylic anions also compete with H₂O₂ and Cl⁻ in complexation of iron. Additionally, it seems that the affinity of carboxilic acids to iron ions is also dependent of the length of perfluoric chain in acid.

The fact that the stabilization of bmim⁺ by perfluoric acids was more significant in the inhibition of the oxidation process with the longer perfluoric chains in acid was not clear to us. The strong delocalization of the negative charge and the elongation of the alkyl chain of PFCA weakened the hydrogen bonding ability. It indicated that the hydrogen bonding between bmim⁺ and PFCA anion was not essential in the stabilization of this ion-pair.

However, C₁₀F₁₉O₂⁻ inhibited oxidation of bmim⁺ to a lesser extent than C₈F₁₅O₂⁻. This is probably connected with specific physico-chemical properties of PFCA.

The larger van der Waals volume of fluorinated chains, combined with the low polarizability of fluorine, makes fluorocarbons not only more highly hydrophobic than corresponding hydrocarbons but also lipophobic. This peculiar arrangement of properties provides a driving force for perfluorinated surfactants into self-organized films, bilayers, and discrete supramolecular systems such as vesicles, tubules and micelles.

It is also known that perfluorinated surfactants have a lower critical micellar concentration than their hydrogenated counterparts, implying a higher stability of the corresponding aggregates [25,27]. The critical micellar concentration (cmc) for perfluoric acids with 6 and 8 carbon atoms in an alkyl chain is significantly higher than the 1 mM used in our experiments, but not necessarily for C₁₀F₁₉O₂⁻ [26]. It indicates interactions of the imidazolium and the iron cations with the perfluoric monomer anion or with premicellar aggregates for two shorter-chain acids, and probably micellar structures for the longer-chain acids.

In the presence of extra electrolytes (IL and iron salt), and acid conditions required for Fenton reaction (pH 3), the concentration of C₁₀F₁₉O₂⁻ probably exceeded the critical micellar level, hence a stronger association of the protons must have taken place [28]. This explains the lesser inhibition of bmimCl oxidation by the longest alkyl chain acid.

3.3. Theoretical study

The theoretical calculation carried out with the Gaussian 03 package showed that a strong associative influence exists between bmim⁺ and perfluorocarboxylic acid.

Our calculations confirm previously presented examinations concerning the properties of the structure of ionic liquids with perfluoric anions [29]. In spite of low concentrations of reagents (1 mM), we observed durable connections formed between imidazolium cations and perfluoric anions of carboxylic acid, which is shown in the change of the electron decay density of the imidazolium fragment in bmim⁺. Table 1 shows a change in electron density of induced compounds formed by ionic association. For bmim⁺ containing C₆F₁₁CO₂⁻ the electron density is about 0.075 on the imidazolium ring, and for the structure of bmim⁺ the electron density is about -0.959.

It seems that bmim⁺ cation structure forms a face-to-face structure with the C₆F₁₁O₂⁻ anion (Fig. 6.). This behavior results

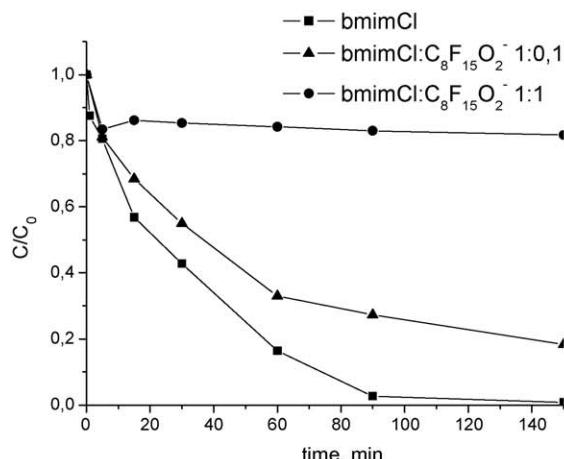


Fig. 5. Decomposition of bmimCl by Fe(III)/H₂O₂ in the presence of C₈F₁₅O₂⁻ (a) and in the presence of C₁₀F₁₉O₂⁻ (b). Experimental conditions: [bmimCl] = 1 mM, [Fe(III)] = 1 mM, [H₂O₂] = 100 mM, pH 3.0.

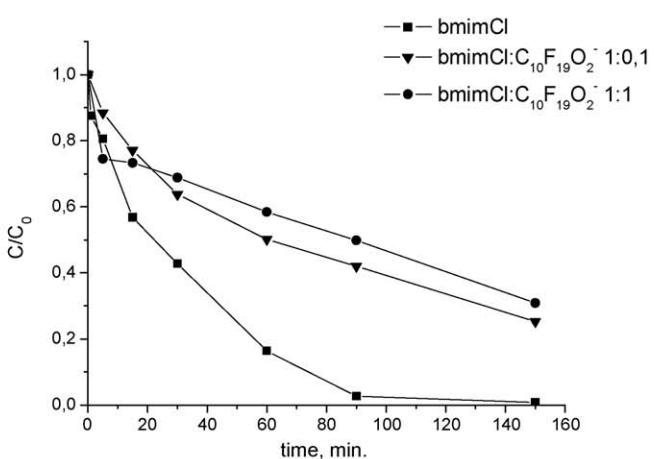


Table 1

Partial charge of the imidazolium ring compared with bmim^+ perfluorocarboxylic acid ion pair from the Gaussian 03 calculation. The atomic number definite to Fig. 7.

Imidazolium ring in bmim^+			$[\text{bmim}^+] [\text{C}_6\text{F}_{11}\text{O}_2^-]$ ion pair		
Atomic number	Atomic symbol	Atomic charge [e]	Atomic number	Atomic symbol	Atomic charge [e]
1	C	-0.845404	1	C	-0.357647
2	N	0.613383	2	N	-0.02102
3	C	-0.217014	3	C	-0.412072
4	C	-0.053933	4	C	-0.107686
5	N	0.57839	5	N	-0.061012
6	C	-1.20838	6	C	-0.421408
7	H	0.459564	7	H	0.233063
8	H	0.328108	8	H	0.236356
9	H	0.29747	9	H	0.186104
10	C	-1.499938	10	C	-0.506848

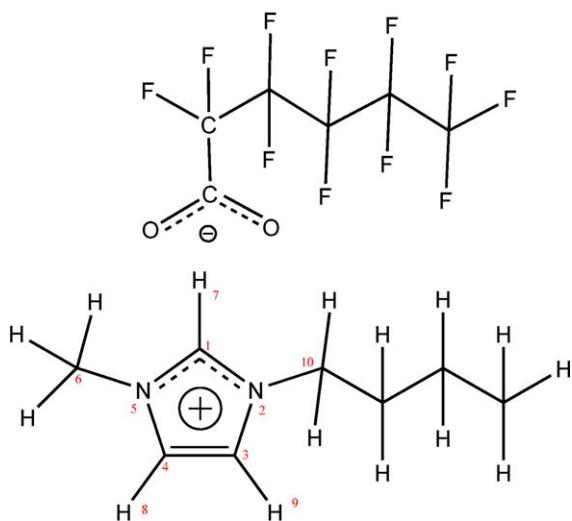


Fig. 6. The structure of BMIM^+ with $\text{C}_6\text{F}_{11}\text{O}_2^-$.

from the fact that the imidazolium ring has a planar structure, interactions between the positive cation and negative anion are very strong and additionally hydrogen bonding which forms a tighter interaction between bmim^+ particles and the $\text{C}_6\text{F}_{11}\text{O}_2^-$ anion (Fig. 7). However, the experimental results suggested that the bmim^+ probably competed with the solvent for hydrogen bonding with perfluoric anion and it could be a reason why hydrogen bonding was not essential for the stabilizing of bmim^+ in water.

4. Conclusions

The modification of the anion led to changes in the physical and chemical properties of the ionic liquids, and as it was supposed, the effect of the counter ion on chemical degradability was generally pronounced. Additionally, the influence of background organic anions, which could be found in wastewater as a result of the application of ionic liquids, may have been of great importance in the choice of these pollutant utilization methods. The rate of bmim^+ degradation in Fenton-like systems is influenced by the anions as follows: $\text{Cl}^- > \text{C}(\text{CN})_3^- > \text{CF}_3\text{SO}_3^-$. A comparative study of three 1-butyl-3-methylimidazolium salts leads to the conclusion that the rate of bmim^+ degradation falls when the counter ions compete with imidazolium cation for hydroxyl radicals, or may undergo complex reactions with ferric and ferrous ions. Additionally, we have clearly shown that the presence of fluorinated organic anions $\text{C}_6\text{F}_{11}\text{O}_2^-$, $\text{C}_8\text{F}_{15}\text{O}_2^-$ and $\text{C}_{10}\text{F}_{19}\text{O}_2^-$ in a bmimCl solution significantly inhibited the degradation process of imidazolium IL by strong interactions between the positively charged imidazolium ring and negatively charged perfluoric acids. For the ionic liquid solution containing $\text{C}_6\text{F}_{11}\text{O}_2^-$ or $\text{C}_8\text{F}_{15}\text{O}_2^-$ ions, the rate of bmim^+ degradation fell due to the increased strength of the interaction between ions. The interaction between bmim^+ and $\text{C}_8\text{F}_{15}\text{O}_2^-$ ion is stronger than that of bmim^+ and $\text{C}_{10}\text{F}_{19}\text{O}_2^-$ ion, as the concentration of $\text{C}_{10}\text{F}_{19}\text{O}_2^-$ is probably near the critical micellar concentration and a stronger association with the protons could take place. Additionally, the perfluorocarboxylic anions probably protect against complexation of Fe^{3+} by Cl^- , and this leads to an increase in the oxidation rate of bmim^+ in the first 20 min of reaction.

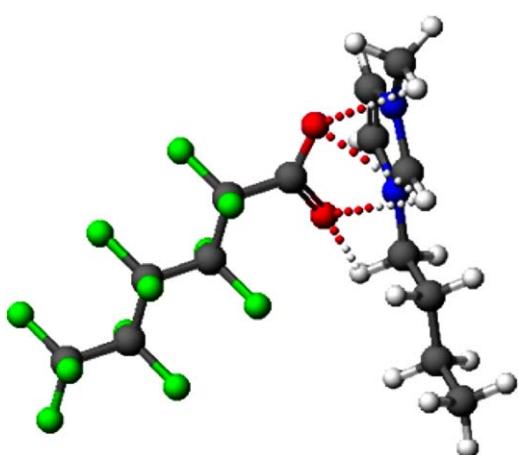
Acknowledgments

We thank Dorota Płotka and Iwona Biesik for help in laboratory work. Financial support was provided by the Polish Ministry of Research and Higher Education under grants: BW 8000-5-0135-8, BW 8000-5-0261-9, DS 8270-4-0093-9 and DS 8200-4-0085-9.

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Fig. 7. The structure of bmim^+ cation face-to-face with perfluorocarboxylic acid calculated with a Gaussian 03 program.



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